A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil

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A B S T R A C T

The oil produced by the pyrolysis of biomass has potential for use as a substitute for fossil fuels. However, the oil needs to be upgraded since it contains high levels of oxygen, which causes low caloric value, corrosion problems, and instability. Generally, upgrading the pyrolysis oil involves the addition of a catalyst, solvent and large amount hydrogen, which can cost more than the oil itself. In this regard, the co-pyrolysis technique offers simplicity and effectiveness in order to produce a high-grade pyrolysis oil. Co-pyrolysis is a process which involves two or more materials as feedstock. Many studies have shown that the use of co-pyrolysis is able to improve the characteristics of pyrolysis oil, e.g. increase the oil yield, reduce the water content, and increase the caloric value of oil. Besides, the use of this technique also contributed to reduce the production cost and solve some issues on waste management. This article tried to review the co-pyrolysis process through several points of view, including the process mechanism, feedstock, the exploration on co-pyrolysis studies, co-pyrolysis phenomena, characteristics of byproducts, and economic assessment. Additionally, several outlooks based on studies in the literature are also presented in this paper.

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1. Introduction

The decrease of fossil fuel resources such as coal, petroleum, and natural gas has encouraged research to develop new approaches to find or invent renewable fuel. One article has predicted that the coal reserves will be available until at least 2112, and it will be the sole fossil fuel in the world after 2042 [1]. Several efforts are currently underway to find alternative energy sources and develop technologies which have high efficiency and are environmentally-friendly. In this regard, most of the effort has been contributed by research into biomass energy. During the last three decades, more than half of the global research has been focused on biomass as renewable energy (56%), followed by solar energy (26%), wind power (11%), geothermal energy (5%), and hydropower (2%) [2]. The high percentage of research into biomass energy can be supported by the availability of biomass resources which are the world's largest sustainable energy source and represent approximately 220 billion dry tons of annual primary production [3].

Beside the effect of decreasing of fossil fuels, environmental concerns also play an important role in the development of renewable energy. The risk and reality of environmental concerns

have drastically increased globally and become more apparent during the past decade, particularly after Earth Summit '92 [4]. Acid rain, ozone layer depletion, and global climate change are negative effects that have resulted from the increase in environmental problems which are due to the emissions of primary pollutants (sulfur dioxide, oxides of nitrogen, hydrocarbons, and carbon monoxide), and are mainly produced by fossil fuel combustion [5,6]. To minimize environmental concerns, it is necessary to consider controlling the pollutant emissions. The optimal use of renewable energy resources can be an optional solution since it significantly contributes to decreasing the negative environmental impacts, reducing the dependence on the use of fossil fuels, and is followed by an increase of net employment and the creation of export markets [2].

There are numerous alternative energy sources available worldwide which can be used to substitute fossil fuels. It is particularly important to consider selection of the proper alternative energy through several factors such as the availability of the source, economic benefit, and environmental benefit. In this respect, biomass is one of the potential sources that can respond to all of the challenges of factors. Biomass is very abundant and can be easily found in diverse forms such as agriculture residues, wood residues, dedicated energy crops and municipal solid waste [7]. Bildirici [8] studied economic growth and biomass energy in the 10 selected

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developing and emerging countries. The author concluded that biomass energy is a stimulus for economic growth and contributes to poverty reduction in developing countries because it meets the energy needs at all times and for all countries, without any expensive conversion devices. Furthermore, the use of biomass as an energy source has been proven to have environmental benefits since it has been determined as a carbon-neutral energy source [9].

Biomass is widely accepted as a potential source of energy and is the only renewable energy source that can be converted into several types of fuels, including liquid, char, and gas, which also promise flexibility in production and marketing. Pyrolysis is generally chosen as a recommended process to achieve this goal. This process has received more attention recently because it can produce the highest liquid yield of up to 75 wt% with conditions of moderate temperature (∼500 °C) and short hot vapor residence time (∼1 s) [10,11]. Nevertheless, the yield of other products also can be optimized by adjusting the parameters of operating conditions. The liquid from the pyrolysis process is known as pyrolysis oil or bio-oil, and has potential as use for fuels or feedstock for many commodity chemicals. In terms of fuels, Bridgwater et al. [12] noted that without an upgrading process, the oil can be directly used in many applications including boilers, furnaces, diesel engines, and turbines for the generation of electricity. In addition, the greatest advantage of pyrolysis oil compared with fossil fuel is that the use of this oil has received positive comments as a more environmentally-friendly fuel because it contributes minimally to the emission of greenhouse gases [13].

Despite the oil from pyrolysis being environmentally-friendly, the fuel characteristic of it remains lower than fossil fuel, especially with regard to combustion efficiency. In this case, the high composition of oxygenated compounds in pyrolysis oil is responsible for this problem. Several researchers have reported that oil from the pyrolysis of biomass generally contains an oxygen content of around 35–60 wt% [11,12,14,15]. It can be identified in the form of more than 200 different compounds in the oils, and is mostly found as water [14]. However, the high level of oxygen in pyrolysis oil creates a low caloric value, corrosion problems and instability [16].

Improvement in the quality of pyrolysis oil is important to assist and provide a solution for several challenges in its applications; therefore, efforts to eliminate the oxygen content are becoming a priority. Many studies have been undertaken to achieve this goal through upgrading techniques. Among them, catalytic cracking and hydrodeoxygenation (HDO) are the most commonly used techniques. Catalytic cracking is a method that involves the addition of a catalyst to the pyrolysis process. This method can be divided into two options: off-line catalytic cracking (using bio-oil as raw material) and on-line catalytic cracking (using pyrolysis vapors as raw material) [17]. Zhang et al. [18] have determined that catalytic cracking is a cheaper method than HDO, but the results do not seem promising because of high coke production during the process (8–25 wt%) and the poor quality of the fuels obtained. Moreover, according to Scheirs [19], there are also some problems associated with the use of a catalyst in the pyrolysis process:

– The catalyst is a consumable and therefore adds to the running cost.
– The catalyst can have a short life-cycle due to poisoning/ deactivation.
– The catalyst leads to increased levels of solid residue, which require disposal.

Furthermore, HDO is an upgrading method that is suitable for converting low-grade pyrolysis oil into hydrocarbons [20]. This process has received a lot of attention because of the significant

increase in hydrocarbon fuel obtained [21]. However, the method is complex and costly because of the complicated equipment, the need to add catalysts, and the high-pressure requirements for the reaction. Thus, a new approach is necessary to overcome this cost. This is discussed further below.

Several comprehensive reviews have been published regarding the pyrolysis of biomass for liquid production. Some review articles have also reported the use of upgrading techniques to improve oil quality. However, reviews on the co-pyrolysis technique for liquid fuel production have not been found. This paper is the first review that aimed to explore the co-pyrolysis of biomass for producing a high-grade pyrolysis oil. The discussion in this review emphasizes the use of biomass waste in the co-pyrolysis process. The use of coals, catalysts, solvents, and any additional pressure in the process was beyond the scope of this review for extraction and analysis. In addition, some of the relevant discussions regarding the excellent features of co-pyrolysis are also presented in this manuscript.

2. Importance of the co-pyrolysis process

Simplicity and effectiveness are especially important in developing a technique to produce the ideal synthetic liquid fuel. In this regard, the idea of co-pyrolysis of biomass can be an optional technique that shows promise by meeting these two criteria. Co-pyrolysis is a process which involves two or more different materials as a feedstock. Many studies have shown that the co-pyrolysis of biomass has successfully improved the oil quantity and quality without any improvement in the system process. In contrast to catalytic cracking and HDO, co-pyrolysis has shown promise for future application in industry because of its attractive performance/cost ratios.

The successful key of this technique mainly lies with the synergistic effect which comes from the reaction of different materials during the process. A previous study has shown that the yield of oil obtained from incorporating plastic was higher than that obtained with woody biomass alone and also had a higher caloric value, which comes from hydrocarbon polymers consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable gas with a high calorie value [22].

The idea of blending oil from biomass with oil from plastic (or waste tire) seems impossible, and may increase operation costs. Oil from biomass cannot be completely mixed with oil from plastic or waste tire because of the polar nature of pyrolysis oil of biomass. If these oils are mixed together, an unstable mixture forms, which breaks (phase separation) after a short period of time. If pyrolysis of biomass and plastic (or waste tire) occurs independently or separately, more energy is required and the cost for oil production will significantly increase. The co-pyrolysis technique is found to be more reliable to produce homogenous pyrolysis oil than the blending oil method. The interaction of radicals during the co-pyrolysis reaction can promote the formation of a stable pyrolysis oil that avoids phase separation [23]. Önal et al. mentioned that several reaction radicals during co-pyrolysis can be formed as follows: initiation, formation of secondary radicals [depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffin and dienes), isomerization via vinyl groups], and termination by disproportionation or recombination of radicals [24].

Furthermore, the main benefit of using co-pyrolysis method is the fact that the volume of waste can be reduced significantly as more waste is consumed as feedstock. It also has the added benefits of reducing the landfill needed, saving costs for waste treatment, and solving a number of environmental problems. Since the disposal of waste in landfills is undesirable [25], this method

could be proposed as an alternative waste management procedure for the future that will have a significant impact on waste reduction and may enhance energy security. In addition, from an economic point of view, co-pyrolysis has been found to be a promising option for a biomass conversion technique to produce pyrolysis oil. Kuppens et al. [26] investigated the economic consequences of the synergetic effects of flash co-pyrolysis. They concluded that the use of co-pyrolysis techniques is more profitable than pyrolysis of biomass alone and that it also has potential for commercial development.

3. Mechanism of the co-pyrolysis process

The mechanisms of co-pyrolysis and normal pyrolysis are almost the same. Basically, the process is performed in a closed reactor system with moderate operating temperatures and in the absence of oxygen. For the purposes of oil production, there are three basic steps required for the co-pyrolysis process: preparation of samples, co-pyrolysis, and condensation. Fig. 1 illustrates the steps used in co-pyrolysis to produce oil. Prior to co-pyrolysis, the samples should be dried and ground. The drying process can be performed using the oven method (temperature at 105 °C for 24 h). For industrial application, the heat demand for feedstock drying can be covered by internal heat sources through process integration. Researchers suggested that the byproducts char or gas can be combusted to provide the necessary heat for endothermic pyrolysis and other intermediate processes, such as biomass drying [27,28]. The main aim of the drying process is removing the moisture content of sample. High moisture content in feed results in the oil product having a high water content; therefore, Bridgwater [29] suggested that the maximum moisture content in the dried feed material should be 10%. The dried samples also benefit from the grinding process, and small biomass particles with a size of less than 2-3 mm are needed to achieve high biomass heating rates [29].

As can be seen from Fig. 1, there is an optional feature in the co-pyrolysis process: inert gas. Inert gas is used to accelerate sweeping vapors from the hot zone (pyrolysis zone) to the cool zone (condenser). Short hot vapor residence times of less than 2 s are needed to minimize secondary reactions and maximize oil yield [29]. In application, nitrogen (N_2) is an inert gas that is commonly used since it is found to be cheap compared to others. Many studies have proven that the use of inert gases in the pyrolysis process has an effect on liquid yield [30–33]. The proper setting of the inert gas flow rate is needed to attain maximum oil yield, while very high flow rates of inert gas actually decrease the total oil yield. However, the use of inert gas is dependent on the type of reactor used. The fluid bed reactor, circulating fluid bed reactor, and entrained flow reactor are the types which need a high flow rate of inert gas [34]. For vacuum and ablative reactors, the use of inert gas is not compulsory. For ablative reactors, according to Bridgwater and Peacocke, nitrogen purging and the use of any inert gases is not required, but is included in the laboratory tests for control purposes, to ensure safety in the feeder and residence time control in the reactor [35].

Furthermore, the pyrolysis process is also influenced by many parameters, including the type of biomass, temperature, heating rate, reaction time, and particle size of feed. Detailed discussions of the effect of parameters on optimum oil yield in the pyrolysis of biomass have been thoroughly reviewed by Akhtar and Amin [36]. For co-pyrolysis, as a general rule, temperature can be adjusted within the range of 400–600 °C to maximize the production of oil. In this temperature range, more than 45 wt% oil can be produced. However, the optimum temperature required to produce the maximum oil yield is dependent on the characteristics of feedstock. Therefore, characterization with regard to thermogravimetric analysis should be performed to obtain an overview of the thermal behavior of material [37].

Condensation is an important step in the production of pyrolysis oil. Without this step, only the char and gas products can be obtained from the process. The vapors generated during the process pass through the condensation unit to change the physical state of matter from the gas phase into the liquid phase. Vapor product residence time in the reactor can be controlled by the addition of inert gas. Bridgwater [38] noted that pyrolysis vapors can be characterized as a combination of true vapors, micron-sized droplets and polar molecules bonded with water. Rapid cooling of the pyrolysis vapors is required to produce a high liquid yield. The lower vapor temperature (<400 °C) leads to secondary condensation reactions and the average molecular weight of the liquid product decreases. Thus, the temperature in pipelines from the pyrolysis unit to the condensation unit should be maintained at >400 °C to minimize liquid deposition; also, blockage of the equipment and piping system should be avoided [12].
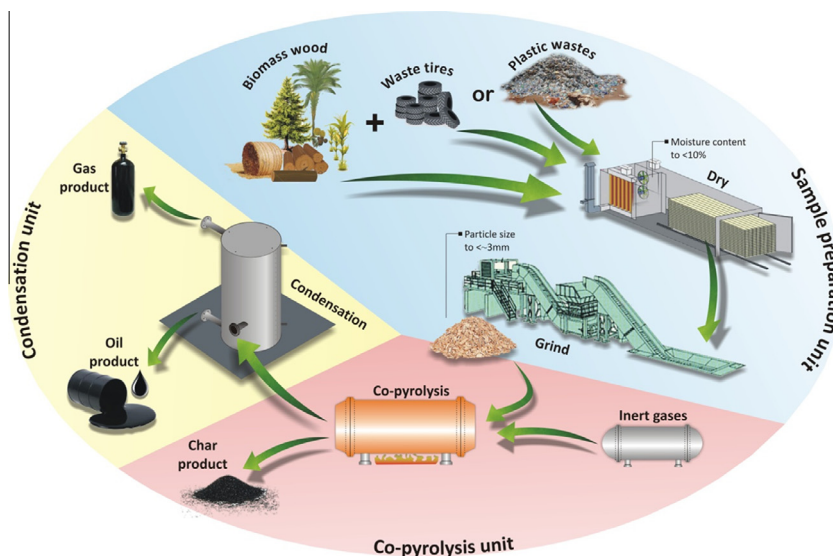

Fig. 1. Co-pyrolysis of biomass.

In contrast to normal pyrolysis, co-pyrolysis has a special parameter which is called the ratio of feedstock. According to researchers, this parameter is very important since it has a significant effect, leading to the production of extra oil. Sharypov et al. [39] conducted a study into co-pyrolysis of wood biomass and a synthetic polymer mixture. Their study concluded that the most important parameter for liquid production is the biomass/plastic ratio in the feedstock. The same tendency was also found by Abnisa et al., who performed a study into co-pyrolysis of palm shell and polystyrene waste mixtures for the synthesis of liquid fuel [40]. Their study included screening three effective parameters (temperature, feed ratio, and reaction time) and an optimization study using response surface methodology. Their results showed that the ratio of feed was the most significant variable affecting liquid yield production.

The type of reactor used also has a large function in the co-pyrolysis process. Bridgwater et al. highlighted the critical features of successful pyrolysis reactors, which have been defined as very high heating rates, moderate temperatures, and short vapor product residence times for liquids [12]. Several comprehensive reviews have been published to explore the type of pyrolysis reactor for liquid production [28,29,34,41,42]. Each reactor has known advantages and disadvantages in operation and scaling. For fast pyrolysis, the fluidized bed reactor is recommended because of its relative ease of scalability and simple operation compared with other reactor types. Most studies on co-pyrolysis were performed using a fixed-bed reactor [24,43–47]. Fei et al. noted that the extent of contact between the used feedstock is an important factor to achieve the synergistic effect; therefore, the synergistic effect is more likely to occur when pyrolysis is carried out on a fixed-bed reactor than on a fluidized-bed reactor [48]. However, a new research finding in 2014 stated that the auger reactor is more effective for co-pyrolysis. Martinez et al. [23] performed the co-pyrolysis of biomass and waste tires using two different reactors, namely, the fixed-bed reactor and auger reactor. The results of their comparison study showed that the auger reactor produces more liquid yield than the fixed-bed reactor for the 90/10 of biomass/waste tire blend. The experimental results from the auger reactor also revealed a remarkable upgrade for some liquid properties, such as lower total acid number, lower density, higher pH, higher calorific value, and lower oxygen content.

4. Feedstock for the co-pyrolysis process

A diversity of renewable energy resources can be found around the world, including biomass energy, wind energy, solar energy and geothermal energy. Among these, biomass is the only source of renewable energy that can produce fuels in the form of solid, liquid and gas, through assistance of the pyrolysis process. Although fuels from biomass, especially wood-based biomass, typically have a lower energy content than fossil fuels, the use of co-pyrolysis technology is improving this condition. In this section, the discussion only focused on the selection and availability of feedstock which can potentially be used in the co-pyrolysis process.

4.1. Selection of feedstock

Some types of biomass have the potential for use in the co-pyrolysis process to improve the quality and quantity of pyrolysis oil. In this regard, the selection of biomass wastes is becoming an important issue requiring study. Currently, many kinds of biomass have been successfully used as feedstock in the co-pyrolysis process in research, which can be categorized into four groups:

agricultural residues, wood residues, municipal solid wastes (MSW) and dedicated energy crops. The list of feedstock types is shown in Table 1. From the list it can be seen that most feedstocks are dominated by MSW. Therefore, it can be noted that co-pyrolysis plays an important role in MSW treatment management. Zaman [49] studied the comparison of MSW treatment technologies using the life cycle assessment method. The author reported that although the sanitary landfill has a good impact on the environment, there are some major problems, such as photochemical oxidation, global warming and acidification, which are still not solved. However, pyrolysis is comparatively more favorable to the environment since it can address the global warming, acidification, eutrophication and eco-toxicity categories. Also, it has higher energy recovery efficiency compared to other thermal technologies.

As can be seen from Table 1, the use of biomass as a material in co-pyrolysis studies varies widely. Among of the various sources, plastic is one of the biomass types that is commonly used in co-pyrolysis to produce pyrolysis oil. Plastics are largely synthetic materials, made from an extremely inexpensive, but nonrenewable resource, crude oil (see Fig. 2) [72]. Because of its origin, plastic contains hydrogen and carbon; thus, it can be pyrolyzed into hydrocarbon fuels. In plastics pyrolysis, the macromolecular structures of polymers are broken down into smaller molecules or oligomers and sometimes into monomeric units. Further degradation of these subsequent molecules depends on a number of different conditions including (and not limited to) temperature, residence time, and the presence of catalysts and other conditions [22]. The liquid product from pyrolysis of plastic has a competitive calorific value compared to conventional fuels, which were around 40 MJ/kg. Therefore, the presence of plastic in the pyrolysis of other biomass types can make a positive contribution to the heating value through synergy.

Another material with similar characteristics to plastics is tires. Tires are primarily made from rubber (60–65 wt%) and carbon black (25–35 wt%), with the rest consisting of accelerators and fillers, which are added during the manufacturing process. Many different synthetic and natural rubbers are used, e.g. styrene–butadiene rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber and polybutadiene rubber. Generally, synthetic rubber is made by the polymerization of a variety of petroleum-based precursors called monomers, while natural rubber comes from the *Hevea* tree [73]. Pyrolysis of tires can produce the oil, char and gas yields of 25–75 wt%, 26–49 wt%, and 5–57 wt%, respectively, depend on parameter settings. According to Martínez et al. [73], oil produced from the pyrolysis of tires can reach an energy content of up to 44 MJ/kg. Oil containing a very low level of oxygen has a high H/C atomic ratio (around 1.5), and consists of aliphatic and aromatic compounds.

Petroleum is a valuable and finite natural resource. More than 70% of petroleum is used in the transportation sector [74]. When petroleum is used as a transport fuel, this means that petroleum is the end product; as consequence, the world may run out of petroleum. Nevertheless, some petroleum is still stored in other forms, such as plastics and tires. Since plastics and tires have the same important properties as fuel, these wastes require extra attention with respect to management. The wastes can be used further to produce second-generation biofuels through pyrolysis. However, not all wastes need to be converted into fuel, because a proportion of them can be sent for recycling into new products. In this regard, the efficiency of the consumption of plastic or tire wastes for liquid fuel production should be considered. In terms of improvements in the efficiency of consumption, the co-pyrolysis process can be used as an option.

Table 1
Type of biomass used in co-pyrolysis process research to obtain liquid products.

Types of biomass	Biomass
Agricultural residues	Pine cone [50], corn residues (cobs and stover) [51], sugarcane bagasse [52], cattle manure [53], rice husk [54], corn stalk [55], wheat straw, oat straw [56]
Wood residues	Beech wood [39], pine wood [39], fir sawdust [45]
Municipal solid wastes (include industrial wastes)	Palm shell [40], potato skin [44], waste electrical and electronic equipment [45], polystyrene waste [40], sewage sludge [57], wheat straw [57], legume straw [58], walnut shell [59], scrap tires [60], recycled plastic [60], hazelnut shell [61], LDPE waste [62], olive pomace [63], polypropylene waste [64], polyethylene waste [65], PVC waste [66], carpet disposal, residues of paper, residues of plastic/metal/drinking cartons sorting installation [37], HDPE waste [67], apricot [68], jatropha cake [69].
Dedicated energy crops	Rapeseed [57], switchgrass [70], sorghum [55], willow [71]
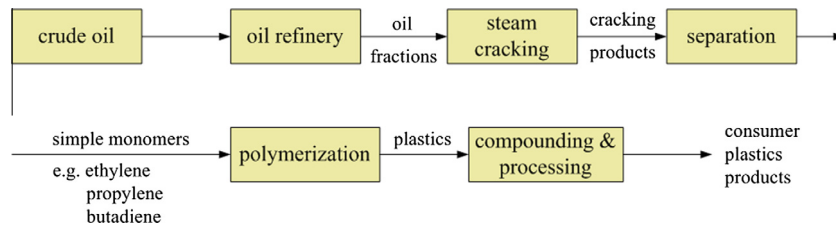
Fig. 2. Actual production flow-chart of plastics [72].

4.2. Availability of feedstock

An important criterion for selecting the proper materials as alternative energy sources is its availability. In this context, biomass has been found to be sufficient for meeting this criterion. Biomass can be obtained from forestry residues, agricultural residues, agro-industrial wastes, animal wastes, industrial wastes, sewage, municipal solid wastes, and food processing wastes; thus, as consequence, the total accumulation of biomass will always be high. Each country has different sources of biomass depending on a number of factors such as geographical conditions, population levels, economic development, agricultural development, forest development, industrial growth, food demand and lifestyle. This means that all of the countries in the world have the same opportunities with regard to the co-pyrolysis process for the production of liquid fuel from biomass.

Furthermore, the availability of plastics as a feedstock is confirmed as being sufficient for the future sustainability of pyrolysis oil production. Plastics are globally available in an abundance. A report released by PlasticsEurope (Association of Plastics Manufactures) mentioned that the global plastics production has increased every year since 1950 [76]. The total global plastics production has grown from around 1.7 million tons (MT) in 1950 to 265 MT in 2010. An estimation of the global plastic production in 2009 and 2010 is shown in Table 2. However, the high production of plastics has a linear relationship with increased end-of-life plastic. In 2009, around 43.6% of total plastic production was considered waste in Europe and the amount was increased by around 3% in the next

year. Thus, there is room for further use of this material in order to minimize the disposal of valuable plastics in landfills.

Around 1.5 billion tires are produced worldwide every year, which will eventually be categorized or interpreted as waste tires [79]. An overview of tire production for several countries in 2006 and 2007 is shown in Table 3. Waste tires are known to have a significant impact on increasing the urban waste stream and it will become a major threat to the environment. Approximately 64% of waste tires are sent to landfill or illegally dumped or stockpiled, with only 13% of them being recycled [80]. In landfills, waste tires are not easily degraded, but tend to float to the top over time due to trapped gases, thus breaking landfill covers. The incineration of waste tires requires the expensive control system of air emissions because this process produces toxic gases, which contain carcinogenic and mutagenic chemicals. Special treatment and attention are needed to tackle waste tires, and pyrolysis has been found to be a technically feasible way to treat tires and recover valuable products.

Wastes of plastics and tires are considered to be potential sources to use as a co-feed in co-pyrolysis to produce liquid fuel. As well as those materials having high energy content, the sources

Table 2
Estimation of the global plastic production in 2009 and 2010 [75,76].

Countries	Yearly production (MT)	
	2009	2010
China	34.50	62.28
Europe	55.20	56.98
NAFTA	52.90	54.33
Rest of Asia	37.95	39.75
Middle East and Africa	18.40	17.23
Latin America	9.20	13.25
Japan	12.65	13.25
CIS	6.90	7.95

Table 3
Estimation of tire production for several countries in 2006 and 2007 [77,78].

Countries	Yearly production (in thousands of units)	
	2006	2007
China	274,230	336,700
U.S	200,281	195,000
Japan	175,916	176,207
South Korea	81,508	85,853
Germany	75,342	75,218
France	59,000	61,300
Brazil	42,216	Not available
Indonesia	41,300	44,300
Russia	40,417	42,330
India	32,880	33,695
Canada	30,216	33,303
Italy	32,017	31,140
Poland	28,931	30,747
Thailand	26,931	Not available
Turkey	23,905	25,795
Romania	14,761	16,600
Malaysia	11,560	13,420

are particularly easy to find and available in huge amounts in all countries around the world. Pyrolysis of the blends of those materials with other biomass wastes will encourage the creation of innovative new concepts in waste management, energy security enhancement, and environmental concerns. Therefore, it is important to note that development of the co-pyrolysis process to produce liquid fuel may be applicable in most countries.

5. Exploration of co-pyrolysis studies

The exploration of co-pyrolysis studies is necessary in order to generate ideas with regard to producing high-grade pyrolysis oil. For this reason, many efforts have been made by researchers to explore this technique, and have revealed many interesting findings. An overview of studies of the co-pyrolysis of biomass wastes with emphasis on pyrolysis oil production is described below.

5.1. Use of plastics in co-pyrolysis

Most co-pyrolysis studies have selected plastics as one of the co-feeds, with the aim of improving the oil yield in terms of quality and quantity. The summaries of studies on co-pyrolysis of biomass mixed with plastics to produce pyrolysis oil are shown in Table 4. All of the experiments listed in Table 4 were performed without any catalysts, solvents or additional pressure. Abnisa et al. [46] investigated the co-pyrolysis of palm shell and polystyrene (PS) to obtain a high-grade pyrolysis oil. Palm shell is well known as a waste generated from the palm oil mill industry, and is available in huge amounts in Malaysia; around 5.2 MT were produced in 2009. Furthermore, over 280,000 Tons of waste PS is produced annually in Malaysia, most of which is contributed by food packagers. The experimental results showed that by adding the same weight ratio of PS in the pyrolysis of palm shell, the yield of oil increased to about 61.63 wt%, while the pyrolysis of palm shell alone only yielded oil at a level of about 46.13 wt%. The high yield of oil was obtained with a process temperature of 500 °C, a heating rate of 10 °C/min, a reaction time of 60 min, an N_2 flow rate of 2 L/min. Moreover, the quality of oil was improved when PS was involved in the pyrolysis of palm shell. For the pyrolysis of palm shell alone, a high heating value (HHV) of oil product was obtained, of about 11.94 MJ/kg. However, pyrolysis of palm shell mixed with

PS raised the HHV of oil up to 38.01 MJ/kg. Lastly, the authors concluded that the use of palm shell and PS wastes for the recovery of liquid fuel by co-pyrolysis is the key to overcoming environmental problems stemming from the high volume of palm shell waste generated by the palm oil industry; also, it can be noted that this is an optional solution to increasing energy security in Malaysia.

Brebu et al. [50] explored the co-pyrolysis of pine cone with synthetic polymers. The polymers used included low density polyethylene (LDPE), polypropylene (PP), and PS. In their study, pine cones were obtained from a forest in Izmir (Turkey), while commercial polymers of LDPE, PP, and PS were selected which were free from any stabilizers, fillers and pigments. The pyrolysis temperature was 500 °C with a heating rate of 10 °C/min. Liquid was found to be the main product of the experiment and yields varied from 47.5 to 69.7 wt%. The lowest liquid yield was obtained from the pyrolysis of pine cone (47.5 wt%). However, by mixing the pine cone and polymers in the same weight ratio, the liquid yield obviously increased. Furthermore, Brebu et al. also reported that the energy contents of oils from the pyrolysis of mixed materials were higher than those produced by the pyrolysis of pine cone alone.

The utilization of biopolymers in co-pyrolysis has also attracted the attention of some researchers. Cornellissen et al. have performed several studies regarding the use of biopolymers in co-pyrolysis to produce liquid fuel. Several biopolymers that have been tested include polylactic acid (PLA), corn starch, polyhydroxybutyrate (PHB), biopearls, eastar, solanyl and potato starch [71,81,82]. Willow was selected as a representative biomass in their study. The process was performed in a semi-continuous home-built pyrolysis reactor, flushed with nitrogen gas, and the temperature was set around 450 °C (723 K). They found that the flash co-pyrolysis of willow/biopolymers blends generally results in improved pyrolysis characteristics: a synergetic increase in pyrolysis yield, a synergetic reduction of the water content in oil yield, an increase in heating value, and the production of easily separable chemicals. Among them, PHB was found to be the biopolymer with the most potential for use in co-pyrolysis since it can produce the highest oil yield and has the highest heating value.

Some interesting observations can be made from the data obtained, which are presented in Table 4. The presence of plastics in the pyrolysis of biomass has clearly improved the liquid yield. The pyrolysis of mixtures of biomass and plastics is able to produce extra liquid, typically between 1.42 and 22.2 wt%. This finding was

Table 4
Summaries of studies on co-pyrolysis of biomass mixed with plastics.

Ref.	Type of materials		T (°C)	Liquid yield (wt%)			Calorific Value (MJ/kg)	
	Biomass	Type of plastics		Biomass alone	Mixture materials (1:1 weight ratio)	Extra yield	Biomass alone	Mixture materials (1:1 weight ratio)
[46]	Palm shell	PS	500	46.13	61.63	15.5	HHV = 11.94	HHV = 38.01
[50]	Pine cone	LDPE	500	47.5	63.9	16.4	GCV = n.d	GCV = 46.33
		PP	500		64.1	16.6		GCV = 45.58
		PS	500		69.7	22.2		GCV = 46.43
[71]	Willow	PHB	450	49.71	64.24	14.53	HHV = 16.10	HHV = 20.22
[82]	Willow	PLA	450	48.85	51.30	2.45	HHV = 16.13	HHV = 18.49
[44]	Potato skin	HDPE	500	23.00	39.00	16.00	HHV = 32.00	HHV = 45.61
[45]	Fir sawdust	Waste electrical and electronic equipment	500	46.30	62.30	16	Not reported	Not reported
[47]	Wood chip	Block polypropylene	500	39.30	63.10	23.80	HHV = 19.90	HHV = 45.00
[83]	Pine residue	Plastic waste contained: 56% PE, 17% PS and 27% PP	400	32.00	53.00	21	HHV = 20.00	HHV = 45.00
[84]	Cellulose	PS	500	45.50	58.80	13.3	Not reported	Not reported
[85]	Pinewood sawdust	PS	450	46.00	67.00	21	Not reported	Not reported
[81]	Willow	Biopearls	450	50.10	52.79	2.69	HHV = 16.10	HHV = 19.10
		Solanyl			59.24	9.14		HHV = 15.70
		Potato starch			51.52	1.42		HHV = 19.20

also supported by Szuba and Michalik, who mentioned that the increase in the yield of liquid products through co-pyrolysis may vary in the range of 2–23 wt% [86]. At the same time, the energy content of the liquid, represented by the calorific value, showed a significant increase. Based on the data in Table 4, all types of plastics are known to improve the calorific value of the liquid product. However, the concentration of energy produced from the co-pyrolysis of biopolymers was found to be lower compared to the oil produced from synthetic plastics.

5.2. Use of waste tires in co-pyrolysis

There is growing interest among researchers in the use of waste tires as a fuel source through the process of pyrolysis. As a research output, several comprehensive reviews on various aspects of waste tires pyrolysis for liquid production have been published in 2013 [73,79,80]. In co-pyrolysis, many studies of pyrolysis of waste tires mixed with other materials have been carried out. However, studies which focused on the pyrolysis of waste tire/wood-based biomass blends are currently still limited. Therefore, some effort should be made to examine the existence of synergistic effects when employing various pyrolysis conditions for the pyrolysis of waste tire/biomass. Several studies which involved waste tires in the co-pyrolysis process are summarized in Table 5. All of the data summarized in Table 5 were collected from experiments without using catalysts and solvents or any additional pressure.

As can be seen from Table 5, the studies have been classified into two categories: co-pyrolysis of waste tires with wood-based biomass and co-pyrolysis of waste tires with waste oils. In studies of the co-pyrolysis of waste tires with wood-based biomass, the addition of waste tires was used with the aim of obtaining extra oil. From the studies performed by Alias et al. [87] and Cao et al. [43], it is indicated that the presence of waste tires in the pyrolysis of biomass significantly contributes to the increased oil yield. Furthermore, as tire mass is increased in the pyrolysis of biomass, the calorific value of the oil obviously increases. Therefore, co-pyrolysis overcomes a defect of the low calorific value of the oil derived from the pyrolysis of biomass alone.

The second classification in Table 5 is the co-pyrolysis of waste tires with waste oils. For this classification, waste oils were used to improve the quantity and quality of pyrolysis oil from waste tires. This approach is economical and has great potential as an eco-friendly option. Waste oils such as waste lubricant oil, bilge water oil and oily sludge can be categorized as hazardous waste, since these pose an environmental hazard due to both their metal content and the presence of other contaminants. Thus, a proper option to manage waste should be considered, and co-pyrolysis has been suggested as an alternative technology for conversion of these kinds of waste materials for energy recovery and environmental protection. Önenç et al. [88] studied co-pyrolysis of scrap tires with oily wastes and concluded that co-pyrolysis of scrap tires with oily waste could be an environmentally friendly method for the transformation of hazardous waste into valuable products such as chemicals or fuels.

6. Synergistic effects on co-pyrolysis

A synergistic effect is the main factor responsible for all improvements in oil quality and quantity. This phenomenon has been considered an interesting area to be researched by a number of groups. Generally, the research is focused on the study of synergistic effects or the interactive effects between the feedstock used. Some common findings in co-pyrolysis studies are discussed in this section.

6.1. Mechanism of synergistic effects

Synergistic effects can be achieved through radical interactions during the co-pyrolysis reaction. According to Johannes et al. [91], data on the so-called positive or negative synergy depend on the type and contact of components, pyrolysis duration, temperature and heating rate, removal or equilibrium of volatiles formed, and addition of solvents, catalysts, and hydrogen-donors. Among these factors, the types of blending feedstock are a major factor that can significantly influence the synergistic effects; thus, synergistic effects on co-pyrolysis can be complicatedly varied [48].

Liu et al. [45] performed a series of co-pyrolysis experiments at 773 K by varying the blending ratio of the biomass and waste electrical and electronic equipment (WEEE). Fir sawdust was selected as a representative biomass. The authors concluded that a significant increase in the pyrolysis oil yield can be indicated as the occurrence of synergistic effects during the co-pyrolysis process. Subsequently, the authors reported the existence of some mechanisms of synergistic effects, which were clearly observed in their study. One of the mechanisms explained was about hydrogen donors. The biomass has a higher H/C molar ratio than WEEE, and the relatively high hydrogen content in biomass can act as a hydrogen donor to WEEE during co-pyrolysis. A similar finding was also reported by Zhang et al. [92]. Water, one of the major components in biomass pyrolysis, is also expected to act as a reactive compound to promote further cracking of the WEEE tar to produce more volatile compounds, thereby increasing the pyrolysis oil yields.

Furthermore, some researchers contend that knowledge of the synergistic effects remains poor. Zhou et al. [93] commented that the mechanism of the synergistic effect between biomass and plastic during co-pyrolysis is unclear. This opinion was also supported by Wang and Li [94]. Biomass and plastic have different decomposition mechanisms in the thermal pyrolysis process. The pyrolysis of biomass involves a series of exothermic and endothermic reactions [95], whereas the thermal pyrolysis of plastic occurs by a radical mechanism (initiation, propagation, and termination) [24]. Jakab et al. opined that biomass has lower thermal stability than plastics, which can affect their radical degradation mechanism by promoting the degradation of synthetic macromolecules [96,97]. Sun et al. [98] studied the co-pyrolysis of poplar wood and high density polyethylene (HDPE) in a micro-scale reactor using pyrolysis-gas chromatography/mass spectrometry. Their results explained that free radicals are formed from biomass pyrolysis and participate in reactions of plastic decomposition, yielding more light paraffins, because of the lower temperature of biomass component decomposition compared with that of polyolefins. Moreover, Önal et al. [24] described that the synergistic effect in co-pyrolysis is complex because of various chemical species. According to the authors, several reaction radicals can be induced during co-pyrolysis of HDPE and biomass, including initiation, formation of secondary radicals [depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffin and dienes), and isomerization via vinyl groups], and termination by disproportionation or recombination of radicals.

Wang and Li [94] investigated the synergistic interaction potential in the devolatilization characteristics of polylactic acid (PLA) and biomass mixtures during co-pyrolysis. The authors stated that some possible general reactions can be proposed, such as: (1) the decomposition of lignin and/or hemicellulose results in volatiles that react with PLA, which can then additionally react with cellulose; (2) the decomposition of biomass and PLA occurs simultaneously, resulting in interactions during the decomposition of biomass and PLA and/or interactions between volatiles after decomposition of biomass and PLA and/or interactions between

Table 5
Several studies of the use of waste tires in co-pyrolysis.

Classification	Ref.	Materials description	System configuration and operation conditions	Relevant results and observations
Co-pyrolysis of waste tires with wood-based biomass	[87]	Waste tires without wire steel were mixed with empty fruit bunches with a ratio of 1:1	The experiment was performed using a fixed bed reactor. Co-pyrolysis was carried out under a nitrogen atmosphere at a temperature of 500 °C. Pyrolysis oils were collected in an ice/water condenser	The products of liquid, char, and gas were obtained at levels of 42.80 wt%, 33.20 wt%, and 24.00 wt%, respectively. The liquid product was significantly decreased when the empty fruit bunches were pyrolyzed alone without being mixed with waste tires
	[43]	Tire powder with a particle size less than 165 μm mixed with sawdust powder (198–350 μm). The ratios of tire to sawdust in the feed were varied at 0:100, 40:60, 60:40, and 100	Feedstock of 100 g was put into the fixed-bed pyrolysis reactor. Before heating the reactors, they were first blown for 30 min with nitrogen. The reactor was heated to the designated temperature of 500 °C at 20 °C/min and held at that temperature for a minimum of 3.5 h	The liquid yield reached 45.0 wt%, 46.2 wt%, 47.0 wt% and 47.2 wt% when tires mass occupied 0%, 40%, 60% and 100% in the mixture, respectively. The liquid derived from pyrolysis of sawdust alone had a HHV of 28.51 MJ/kg, while the value was increased to 42.44 MJ/kg when tire mass accounted for 60% of the mixture
	[23]	Pine woodchips (15 mm) containing bark and waste tires (5 mm) were used for the experiments	Two reactors with different scales were used in this study. The first part of the co-pyrolysis experiment was carried out in a fixed bed reactor (74 cm length and 1.6 cm internal diameter). The reactor was heated externally at temperature of 500 °C with a heating rate of 80 °C/min. The reaction time was set to 15 min. Different feedstock mixtures on mass basis were studied in the fixed bed reactor: 100% biomass (100/0); 90% biomass and 10% waste tires (90/10); 80% biomass and 20% waste tires (80/20) and 100% waste tires (0/100)	The results from the first part of the experiment showed that the pyrolysis of biomass alone yielded around 50.0 wt% oil, whereas the pyrolysis of tire only resulted in about 47.6 wt% oil. Remarkably, no increase in liquid yield was observed in the pyrolysis of mixtures of pine woodchips and waste tires
			The auger reactor with a pilot plant scale was used for second part of the co-pyrolysis experiment. Experiments were set at 500 °C using nitrogen as a carrier gas at 5 l/min and a mass flow rate of 5 kg/h. The residence time of the feedstock inside the reactor was fixed at 5 min	For the second experiment, the liquid yield was 52 wt% for the pyrolysis of pine woodchips. An increase in the liquid yield was found for the 90/10 blend (56.0 wt%), which was obviously higher than that for the liquid yield obtained from a fixed bed reactor (48.5 wt% for the 90/10 blend)
				The authors noted that the lowest calorific value was obtained for pyrolysis of the biomass, while the highest was obtained for the pyrolysis of tires. In addition, all calorific oils increased with an increased waste tire ratio in the blend
Co-pyrolysis of waste tires with waste oils	[89]	Two different types of scrap tires, passenger car tire (PCT) and truck tire (TT), were mixed with waste lubricant oil (WLO). Both tires were ground to the desired particle size of 1.5–2.0 mm. The scrap tires contained no steel thread or textile netting. Each tire was mixed with an equal ratio of WLO	Co-pyrolysis experiments were carried out in a fixed bed reactor and under nitrogen atmosphere at temperatures of 550, 650 and 800 °C. The reactor was purged before experiments using a nitrogen gas flow of 25 ml/min for 10 min to remove any air inside. Liquid products were condensed in the first two traps by cooling with an ice bath	The addition of WLO in the pyrolysis of scrap tires is aimed at obtaining extra oil. The results showed that co-pyrolysis with WLO produced more oil than pyrolysis of tires alone. Co-pyrolysis of PCT with WLO produced liquid about 67 wt%, while co-pyrolysis of TT with WLO produced a higher liquid yield of about 72 wt%. An increase in the co-pyrolysis temperature had no effect on the oil quantity. The calorific values for co-pyrolysis oils were slightly higher than those of pyrolysis oils and close to those obtained for commercial diesel
	[90]	Scrap tire (ST) with a particle size of less than 2 mm was mixed with oily wastes, including bilge water oil (BW) and oily sludge (OS). The ratios of ST:BW and ST:OS were fixed at 1:1	The pyrolysis experiments were carried out in a fixed bed design and stainless steel reactor (L; 210 mm; Ø; 60 mm) under atmospheric pressure using a semi-batch operation. The co-pyrolysis experiment was performed at 500 °C	The pyrolysis of scrap tires at a temperature of 500 °C produced an oil yield of 44.1 wt%. The increase in oil yield from co-pyrolysis processes of ST:BW and ST:OS was found to be 64.8 and 62.4 wt%, respectively. The HHV of pyrolysis oils was obtained about 43.8, 44.8 and 44.9 MJ/kg for pyrolysis of ST, co-pyrolysis of ST:BW, and co-pyrolysis of ST:OS, respectively
	[88]	Scrap tire (ST) samples were shredded, crumbed and sieved from the sidewall rubber of scrap tires to produce a size of 1.5–2.0 mm. The scrap tires contained no steel thread or textile netting. The average rubber composition of the scrap tires was 35 wt% natural rubber and 65 wt% butadiene rubber. Bilge water oil (BW) and oily sludge (OS) were selected as the oily wastes	A glass reactor with an internal diameter of 30 mm and a total length of 350 mm was used in semi-batch operation under self-generated pressure. Pyrolysis was performed at 400 and 500 °C on individual BW, OS and ST and at 500 °C on a ternary mixture with a BW:OS:ST weight ratio of 1:1:2	All experiments from pyrolysis of the individual components showed that the maximum oil yields were achieved at 500 °C. At 500 °C, the oils were obtained at levels of about 77.5, 71.3 and 39 wt% for the pyrolysis of BW, OS and ST, respectively. The oil yield of co-pyrolysis (BW:OS:ST mixture of 1:1:2) was around 50.5 wt%.

condensables of biomass and PLA; (3) the formation of char as a decomposition product of the biomass may be the main cause for the changes in PLA degradation processes.

6.2. Increase in oil yield

As can be seen from Tables 4 and 5, the co-pyrolysis process has a tendency to increase the oil yield. Although there are many factors that might contribute to increase the oil yield, the nature of biomass is a fundamental factor that determines this. The amount of liquid can be easily predicted (low or high) when the composition of biomass has been measured. The composition of biomass is generally reported in terms of its proximate analysis. Proximate analysis is a method which measures the content of four separately identifiable constituents in a biomass: volatile matter, fixed carbon, moisture content, and ash content [99]. Initially, the analysis is addressed toward coals characterization, and then developed to characterize the biomass sample. In pyrolysis, volatile matter and ash content are the main factors that have an effect on liquid yield production. Numerous researchers have recognized that the presence of volatiles favors the production of a large amount of pyrolysis oil. Asadullah et al. [100] noted that volatile matter is usually converted to bio-oil upon condensation. Omar et al. [101] found that a high volatile content provides the advantages of high volatility and reactivity, which are favorable for liquid fuel production. Ash also plays an important role in determining the proportions of the liquid product of biomass pyrolysis. However, the high ash content (alkali metals) contributes to a decrease in the oil yield, and, as consequence, the char and non-condensable gases are produced in higher yields [41,102]. Therefore, it can be highlighted that biomass with a low ash fraction favors high oil yields, and a high fraction of volatiles favors a higher oil yield.

For wood-based biomass, the result of proximate analysis is highly dependent on lignocellulosic contents. Lignocellulosic compounds include cellulose, hemicellulose, and lignin as primary components, and are generally contained in wood-based biomass. Different types of wood-based biomass have different percentages of lignocellulosic components. Among them, cellulose and hemicelluloses are components which play an important role in generating volatile matter. According to Qu et al. [103], cellulose is more volatile than hemicellulose. Therefore, wood-based biomass with has a high amount of cellulose is potentially able to generate high volatile matter, which leads to an increase in oil yield. Lignin, which is composed of aromatic rings with various branches, decomposes over a wide range of low to very high temperatures with a very low mass loss rate. Therefore, wood-based biomass with a higher lignin content might have a relatively higher char yield. The effects of lignocellulose compounds on the production of volatile matter have been widely studied by many researchers [103–106], the results of which are depicted in Fig. 3.

The proximate analysis of plastics depends on their types. Table 6 shows the results of proximate analyses of plastics taken from the literature. From Table 6, it can be seen that all plastic types have high characteristics of volatile matter, which means that all types of plastic have the potential to produce a high liquid yield through the process of pyrolysis. Among the types of plastic, the value of volatile matter of more than 99.50 wt% was observed for HDPE, LDPE, PS, and polyamide. In the study performed by Demirbas in 2004, three types of plastic wastes (PS, PE, and PP) were pyrolyzed, and the results showed that PS yielded the higher liquid level (89.5 wt%) than PE and PP [115]. The same tendency was also observed by Kiran et al., who studied the recycling of plastic wastes via pyrolysis [116]. The oil yield obtained was about 88.8 wt% at a temperature of 600 °C and a heating rate of 5 °C/min. Detailed products and components of the pyrolysis of several types of plastics have been reviewed by Kaminsky [117].
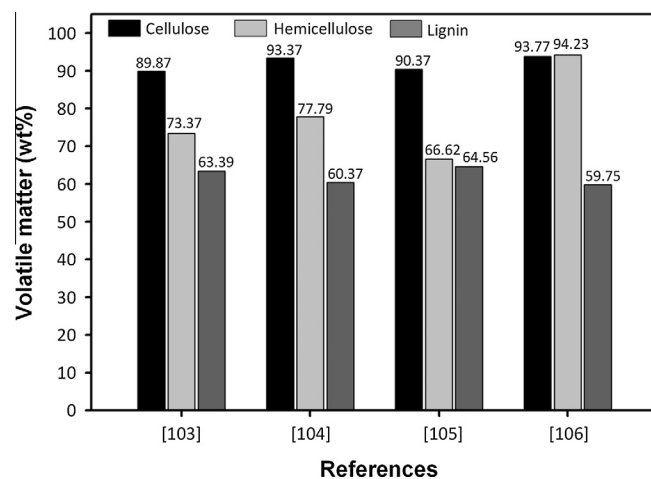

Fig. 3. The definitive trend of biomass composition in producing oil via the pyrolysis process.

According to observations made by Martínez et al. [73], waste tires have volatile matter and ash in the range of 57.50–73.74 wt% and 2.40–20.10 wt%, respectively. The volatile matter of the tire consists mainly of polymeric compounds that come from natural rubber (NR) and synthetic rubber (SR), such as butyl rubber and styrene-butadiene rubber. The proportion of NR and SR are different between passenger car tires (PCT) and truck tires (TT). Generally, the composition of SR was found to be high in PCT, while TT was shown to have a high composition of NR. Ucar et al. [118] performed a study to evaluate two different scrap tires as hydrocarbon sources for pyrolysis. The results of the proximate analysis showed that TT had a higher volatile matter than PCT, while the ash content was found to be higher in PCT. They found that the product distributions from the pyrolysis of PCT and TT were quite different from each other. They also noted that the pyrolysis of TT yielded more liquid than that of PCT.

As described earlier, volatile matter is the key to producing pyrolysis oil. To maximize the generation of volatile matter, it is also important to adjust the parameters controlled in the pyrolysis process. According to Guldogan et al., temperature and heating rate are the pyrolysis parameters which most significantly affect the volatile matter yield [119]. The study performed by Paethanom and Yoshikawa showed that moderate temperature conditions favor the generation of volatile matter [120]. They analyzed the generation of volatile matter at three different temperatures (600, 800 and 1000 °C), and the results showed that the highest volatile matter was obtained at 600 °C, while higher pyrolysis temperatures resulted in higher fixed carbon contents. A similar trend was also found by Azeez et al. [121] who studied the temperature dependence of fast pyrolysis volatile products from European and African biomasses. The experiment was carried out at temperatures between 300 °C and 700 °C with an interval of 50 °C. The results revealed that most volatile products were obtained at 450 °C and 500 °C. Furthermore, Pan et al. [122] explained that the faster the heating rate, the higher the volatile yield in pyrolysis.

6.3. Improvements in oil quality

Synergistic effects also significantly influence improvements in the quality of the oil obtained. These improvements can be clearly seen, especially with regard to fuel properties. Generally, the oil obtained from the pyrolysis of wood-based biomass alone has a lower calorific value, due to the high oxygen content. However, this can be solved by using the co-pyrolysis technique. From Tables 4 and 5, it can be seen that the oil obtained from co-pyrolysis

Table 6
Proximate analysis of plastics.

Type of plastics	Plastics type marks	Moisture (wt%)	Fixed carbon (wt%)	Volatile (wt%)	Ash (wt%)	Ref.
Polyethylene terephthalate (PETE)	♳ PETE	0.46	7.77	91.75	0.02	[107]
		0.61	13.17	86.83	0.00	[108]
High-density polyethylene	♴ HDPE	0.00	0.01	99.81	0.18	[109]
		0.00	0.03	98.57	1.40	[108]
Polyvinyl chloride (PVC)	♵ V	0.80	6.30	93.70	0.00	[110]
		0.74	5.19	94.82	0.00	[108]
Low-density polyethylene	♶ LDPE	0.30	0.00	99.70	0.00	[111]
		–	–	99.60	0.40	[112]
Polypropylene	♷ PP	0.15	1.22	95.08	3.55	[113]
		0.18	0.16	97.85	1.99	[108]
Polystyrene	♸ PS	0.25	0.12	99.63	0.00	[46]
		0.30	0.20	99.50	0.00	[111]
Polyethylene (PE)	♹ OTHER	0.10	0.04	98.87	0.99	[113]
Acrylonitrile butadiene styrene (ABS)		0.00	1.12	97.88	1.01	[114]
Polyamide (PA) or Nylons		0.00	0.69	99.78	0.00	[114]
Polybutylene terephthalate (PBT)		0.16	2.88	97.12	0.00	[108]

showed an increased calorific value. This tendency can be explained by the increased hydrocarbon content of the oil. Therefore, observing the contents of C and H and the H/C ratio is important, since they can significantly control the calorific value. Önal et al. [24] studied bio-oil production via the co-pyrolysis of almond shell and HDPE. The authors noted that liquid products obtained from the co-pyrolysis process had a higher energy content than those of pyrolysis of almond shell alone. This is due to the addition of HDPE to biomass, which increased the H/C ratio from 1.60 to 2.28. They also observed that elemental compositions of co-pyrolysis oils contain higher contents of C and H than pyrolysis oil of almond shell alone. In another study, Martínez et al. [23] studied the co-pyrolysis of pine woodchips with waste tires. The authors reported that the C and H contents in the liquid gradually increased with the proportion of waste tires in the feedstock, while the O content decreased. They noted that a low heating value is the property with the greatest change since it increased from 14.9 to 19.0 and to 25.0 MJ/kg for biomass/waste tire blends of 90/10 and 80/20, respectively. Thus, this showed an increase of up to 27% and 70%, respectively. Although a synergetic effect is observed for both blends, this effect is more significant for the 80/20 blend. From this finding, it can be concluded that the high proportion of waste tire in biomass pyrolysis will contribute more to increasing the heating value.

The high water content of pyrolysis oil contributes to the low energy density; thus, for its utilization as a fuel, this content is undesirable. The water in pyrolysis oil mainly comes from moisture in the feedstock and from dehydration reactions occurring during pyrolysis. According to Wasterhof et al. [123], drying the feedstock to obtain very low moisture levels (approaching zero) leads to a decrease in the water content. The authors also noted that from a practical point of view, such dry feedstock materials are, however, not realistic due to the high costs associated with the dryer. In this regard, the co-pyrolysis technique was found to be effective in controlling the water content of the oil. All wood-based biomass is hygroscopic, meaning that when exposed to air, it will release or pick up moisture until it is in equilibrium with the humidity and temperature of the air; because of this, wood tends to have a high moisture content. Unlike wood, plastics and tires do not absorb much moisture and their water contents are far lower than the water content of wood. Therefore, the reduction of wood proportion and the addition of plastics or tires as feedstock in pyrolysis will contribute to the reduction of water content. Cornellisen et al. [82] performed research with the aim of reducing the amount of pyrolytic water by performing flash co-pyrolysis of willow and polylactic acid. The different blends of willow/polylactic acid with a w/w ratio of 10:1, 3:1, 1:1 and 1:2 were investigate and the authors concluded that the addition of polylactic acid clearly reduced the water content in the oil (up to 37%), which also increased HHV (up to 27%).

Viscosity is an important property in the chemical design process. Viscosity data are essential for various heat transfer considerations, calculating pressure drop, distillation calculations and mixing system considerations. For fuels, viscosity data are used to evaluate the effect on pumping and injecting. From some observations of co-pyrolysis studies, the condition of oil viscosity has not shown a definitive trend. Abnisa et al. [40] reported that liquid from the co-pyrolysis of palm shell and PS mixtures showed higher viscosity compared to the pyrolysis of palm shell alone. The decomposition of inorganic material in PS may have contributed to the higher viscosity. Cao et al. [43] found a different trend with Abnisa et al., and reported that when tire mass was increased in the mixture, the viscosity of the oil gradually decreased. The authors also reported that although the oil showed a decrease in viscosity, it was still higher than that of diesel oil 0#. There is a simple technique that can be used to reduce the viscosity of oil. According to Yu et al. [124], adding methanol and/or ethanol to the pyrolysis oils reduced viscosity and slowed down the increase in viscosity and water content during storage. Blending of methanol or ethanol with pyrolysis oils may be a simple and cost-effective approach to converting pyrolysis oils into a stable gas turbine or home heating fuels.

Generally, the main compounds present in the oil produced by the pyrolysis of wood-based biomasses are alcohols, aldehydes, phenols, acids, esters, ketones, guaiacols, syringols and furans [18]. Among them, phenols have been found to be dominant in

the oil (up to 55%) [125]. According to Samanya et al. [57], the high level of phenols can contribute to increased acidity and instability of the oil. Martínez et al. [23] stated that phenolic compounds originate from the decomposition of lignin contained within the biomass wood. The authors also mentioned that lignin-derived products are mainly responsible for the high molecular weight and viscosity of pyrolysis oils and thus, one of the aims of any upgrading process is to remove these compounds. In this regard, in a study of the co-pyrolysis of biomass with waste tires, Martínez et al. proved that the percentage area of phenolic compounds was significantly decreased for biomass/waste tire blends; this decrease was about 20% and 40% for the 90/10 and 80/20 blends, respectively. Thus, they concluded that a synergic effect toward phenolic compound removal was taking place. A similar tendency was also found by other researchers who studied the co-pyrolysis of palm shell and polystyrene [46]. The authors noted that the quantity of phenol groups in the oil of mixed materials (50:50 ratio) was reduced (around 8.27%) compared to oil obtained from the pyrolysis of palm shell alone, while compounds consisting entirely of hydrogen and carbon were identified as abundant in oil. However, it should be noted that there is a type of plastic which can give a positive contribution to increase the amount of phenols. A research study by Brebu et al. [126] identified abundant phenol compounds in polycarbonate, which has similar characteristics to lignin. The authors noted that the main pyrolysis products from polycarbonate are phenol, with its derivatives at carbon numbers C_{10}–C_{14}, and bisphenol, with its derivatives at C_{22}. In brief, the addition of polycarbonate in the pyrolysis of biomass to produce liquid fuel is not recommended since it can contribute to increase the phenol compounds in the oil.

The co-pyrolysis of biomass wastes has also been found to be effective in recovering hydrocarbon-based chemicals, which promote improvement in the fuel quality. The presence of hydrocarbon-based chemicals has been detected by many researchers through several types of analyses such as GCMS, FTIR, and ^{1}H NMR. Önal et al. [24] reported that co-pyrolysis of HDPE and almond shell led to an increase in alkene fractions by 75% compared with the results obtained for individual biomass pyrolysis. In another study, Aboulkas et al. [127] tried to co-pyrolize HDPE with oil shale. The authors noted that the oil obtained by co-pyrolysis had similar properties to commercial gasoline. In the oil obtained from co-pyrolysis, aliphatic components were dominant. This result was observed using two different analyses: FTIR and ^{1}H NMR. The research article released by Abnisa et al. [46] showed that the hydrocarbon groups in oil from the co-pyrolysis of palm shell and PS were mostly found in the form of aromatics and benzene, with percentages of 39.59% and 32.99%. Cao et al. [43] studied the behavior of co-pyrolysis feedstock between sawdust and tire on the formation of polycyclic aromatic hydrocarbons. The authors reported that the percentage of tire in the mixture had a great influence on the content of polycyclic aromatic hydrocarbons in the oil. The experiment showed that the total content of polycyclic aromatic hydrocarbons varied from 5.78×10^{-4} g g^{-1} to 2.2×10^{-3} g g^{-1} when tire mass occupied 40% and 60% of the mixture, respectively.

The oil from pyrolysis of biomass generally has lower sulfur content at approximately 0.1 wt% [128,129]. The addition of waste tire in the pyrolysis of biomass can increase the sulfur content in the oil. This finding is clearly evident in the study performed by Martinez et al. [23]. The result from ultimate analysis showed an increment in sulfur content when tire mass occupied 10% and 20%. The sulfur content increased by around 0.2 wt% and 0.4 wt% for the 90/10 and 80/20 blends, respectively, whereas no sulfur was detected for pyrolysis of biomass alone. Oil with high sulfur contents needs to be desulfurized before it can be used for combustion. One of the effective techniques that can be applied to remove the sulfur content is the oxidative desulphurization technique. This technique was found to be a very promising approach for the reduction of sulfur content of up to 92%, which only requires low temperature of 50 °C and atmospheric pressure for its process condition [130].

7. Byproducts of the co-pyrolysis process

Furthermore, the co-pyrolysis of biomass wastes also produces char and gas as byproducts. As reported by Bridgwater [29], the byproduct of char from the pyrolysis of biomass is typically obtained in yields of up to 12 wt% on a dry-feed basis, together with gas with a proportion of around 13 wt%. Among the byproducts, gas from the pyrolysis of biomass has a lower calorific value than natural gas or pyrolysis tire gas. However, co-pyrolysis may also increase the calorific value. Some information about the byproducts generated from the co-pyrolysis process is presented below.

7.1. Char

Bernardo et al. [131] studied the physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures. The char samples were obtained from the pyrolysis of three different waste mixtures: plastics, pine biomass, and tire wastes. The authors noted that the addition of tires to the waste mixture significantly increased the yield of char; otherwise, the addition of plastic in pyrolysis of pine biomass had no effect on the increase in char yield. The same tendency was also found by Lopez et al. [132] in a study about the dechlorination of fuels in the pyrolysis of polyvinyl chloride (PVC)-containing plastic wastes. The authors stated that only a small quantity (0.6-1.3 wt%) of solid char was obtained from the pyrolysis of plastics or mixtures of plastics.

In addition, the quality of char from co-pyrolysis showed improvements in the calorific value. Paradela et al. [83] noted that the solid products obtained from the co-pyrolysis of a mixture of materials (biomass and plastic wastes) had higher heating values than some coals. A similar observation was also found in a study of co-pyrolysis of biomass with waste tires, which was performed by Martinez et al. [23]. Similarly, Brebu et al. [50] reported that the char obtained from the pyrolysis of pine cone alone had a lower calorific value than the chars obtained from co-pyrolysis. This is due to the high oxygen content in the char derived from the pyrolysis of pine cone alone. The authors noted that the difference in the elemental composition of chars from synthetic polymers mixed with pine cone and with cellulose may be linked to the presence of lignin in pine cone. Furthermore, the authors also explained that the very low sulfur content was found in chars, making them attractive for use in incineration. This makes these products suitable for use as fuels, e.g. in co-combustion with coal or other wastes. Another application of char is its use as an adsorbent in water treatment to remove heavy metals. The chars formed from co-pyrolysis can also be potentially used as adsorbents through an upgrading treatment. Bernardo et al. [131] performed a multistep upgrading of chars obtained from the co-pyrolysis of PE, PP and PS plastic wastes, pine biomass and used tires. The textural and adsorption properties of the upgraded chars were evaluated and the results indicate that the chars are mainly mesoporous and macroporous materials, with adsorption capacities for methylene blue dye in the range of 3.59–22.2 mg/g. The authors noted that the upgrading treatments performed on the chars allowed carbonaceous materials with sufficient quality to be reused as precursors for adsorbents to be obtained.

7.2. Gas

According to Bridgwater [10], high temperatures and longer residence times were found to be the best conditions to increase the conversion of biomass to gas. Since the process parameters required to maximize oil production are different for gas, in pyrolysis, gas is only obtained in low quantities. Generally, the gas produced by pyrolysis is in the range of 13–25 wt% of the used biomass. Specifically, Kim et al. [133] tried to observe gas production from the pyrolysis of mixed plastics comprised of PE, PP, and PS. The results showed that under normal temperature and pressure conditions, liquid was the main product, with yields of around 75 wt%; gas yield was always lower than 10 wt%. Similar to plastic waste, the pyrolysis of tire also tends to result in a low yield of gas. William [79] tried to summarize the data from several studies related to the pyrolysis of waste tires, and the author found that gas can be obtained in the range of 2.5–28.5 wt%. The author reported that a high yield of gas was usually generated under conditions including a high reaction temperature and a low heating rate. To understand the effect of waste mixture composition on gas production, a study performed by Paradela et al. [83] can be a reference. The authors reported that the increase in biomass percentage led to an overall decrease in the effective liquid yield, while both the solid residue and gas fraction increased almost linearly with the biomass percentage.

The gas composition arising from the co-pyrolysis process is dependent on the composition of the feedstock used. Generally, the gas product released during wood pyrolysis contained CO, CO_2, H_2, CH_4, C_2H_4, C_3H_6, and minor amounts of other hydrocarbons [134]. For the pyrolysis of tires, the main gas components were CO, CO_2, H_2S, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, C_4H_8, and C_4H_{10} [79]. Furthermore, the gas composition in plastics was found to be different depending on the type of plastics. Williams and Williams [135] studied the pyrolysis of six main plastics in municipal solid waste, including HDPE, LDPE, PP, PS, PVC, and poly-(ethylene terephthalate) (PET). The authors reported that the main gases produced from the individual plastics were H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, and C_4H_8 and for the PET plastic CO and CO_2. The presence of hydrogen chloride was only observed and found to be high for the pyrolysis of PVC.

The gas produced from the pyrolysis process has a significant caloric value; therefore, it can be used to offset the total energy requirements of the pyrolysis process plant. Some of the factors that can increase the calorific value are high concentrations of hydrogen and other hydrocarbons. Hester and Harrison [136] reported that at conditions of normal temperature (25 °C) and atmospheric pressure, the calorific value of gas from wood biomass was about 16 MJ/Nm³, while the gas produced from the conventional pyrolysis of municipal waste had a calorific value of the order of 18 MJ/Nm³. The author also noted that the pyrolysis of tire produced a gas with a much higher calorific value, of about 40 MJ/Nm³, depending on the process conditions. In the study of the co-pyrolysis of biomass and plastic waste, Paradela et al. [83] reported on three parameters (reaction time, temperature, and waste mixture composition) which affect the calorific value. Firstly, the authors noted that the increased reaction time increased the gas heating value, due to the increase in the number of alkanes released. Then, the authors noted that the elevated reaction temperature also increased the gas heating value, again due to the increased alkane release. Lastly, the author concluded that the increased biomass content in the waste mixture significantly decreased the gas heating value, mainly due to the decrease in hydrocarbons formation.

8. Economic feasibility assessment

Co-pyrolysis offers simplicity in design and operation, and in many cases has successfully produced oil with a high quantity and quality. Therefore, this technique can play a pivotal role in development of the biomass energy industry. There is an important note which showed that this technique is feasible from an economic point of view. Kuppens et al. [26] used the net present value (NPV) to evaluate the economics of flash co-pyrolysis of 1:1 w/w ratio blends of biomass (willow) and biopolymers (PLA, corn starch, PHB, biopearls, eastar, solanyl, and potato starch). NPV is the best analysis method for selecting or rejecting an investment, either industrial or financial [137–139]. The rule in this analysis was that the project would be accepted if the NPV was greater than or equal to zero, and would be rejected when the NPV was less than zero [140]. In this regard, the study performed by Kuppens et al. showed that flash co-pyrolysis of willow with any biopolymer was economically more interesting than flash pyrolysis of pure willow, because the NPV of co-pyrolysis resulted in positive cash flows for all types of biopolymers used. This result is supported by some other estimations as well, including the initial investment expenditure, the production costs, and the possible revenues. The author also noted that the calculations in this research paper were from a case study in Belgium, but the economic model behind the case study can be adapted to other locations.

In addition, an economic evaluation of the co-pyrolysis process was also studied by Shelley and El-Halwagi [141]. A techno-economic feasibility study was performed to assess the viability of co-liquefying scrap tires and plastic waste into liquid transportation fuels. The return on investment (ROI) approach was used to make investment decisions; if the ROI was positive then the investment was considered profitable. The authors noted that the co-liquefaction of waste plastic and scrap tires as well as the liquefaction of scrap tires alone was both technically and economically feasible. The results showed promising economics for the mixed materials case with an ROI of approximately 18%, as compared to only 12% for the plastics alone scenario. The author also reported that the tipping fees obtained for the raw materials used in the process were the key to overall profitability. Similarly, it is in agreement with another study performed in 1998 by Huffman and Shah [142], who reported that the ROI depends on the tipping fees received for waste plastics and tires. The high tipping fees received will be linearly contributed to the increase in ROI.

9. Discussion on co-pyrolysis scenarios

This review showed that many researchers have studied the potency of co-pyrolysis technique using various types of biomass wastes, and that the results are very encouraging. Different investigations were conducted to obtain oil with a high yield and high quality, which followed the various available standards. Several advantages can be obtained from using this technique such as reducing the consumption of fossil fuels, solving some environmental problems, increasing energy security, and improving waste management systems. Apart from these, this technique also offers simplicity in design and feasibility in regard to economic analysis.

There are some important factors which need to be highlighted in the feed system of the co-pyrolysis process. To obtain a high-grade liquid, adjustments of the types and ratios of feedstock are essential. The suitable combination of feedstock in co-pyrolysis can include wood-based biomass with waste plastic or wood-based biomass with waste tire. Both options are acceptable, since many studies have proven that these combinations can provide improvements in the pyrolysis oil through synergistic effects. However, it should be noted that not all plastic types can be used in the process. PVC is not recommended as a feedstock material because it contains about 57% chlorine by weight, which will affect the diesel quality and can produce chlorinated hydrocarbons, and also because it thermally decomposes to hydrochloric acid, which is very corrosive and toxic. The presence of 1–3% PVC in the

feedstock stream results in the fuel oil product having a total chloride level of 5000–10000 ppm [19].

Furthermore, it is important to note that the main aim of the addition of plastic waste or tire waste in the pyrolysis of wood-based biomass is to improve the quantity and quality of the oil produced. Hence, plastic or tire waste can be called the additive material in the process. In this regard, the proportion of additive material was designed to be less than that of the main feedstock (wood-based biomass). Many studies have shown that a higher ratio of additive material in the pyrolysis of wood-based biomass can contribute to increase the oil quality. However, the minimum use of additive material in each process of co-pyrolysis is preferred; this is due to some considerations such as:

- The production of waste plastics or waste tires in many countries is generally found to be lower than the generation of wood-based biomass. Thus, the limited source of additive material is expected to be used and should be sufficient for the amount of wood-based biomass available.
- Besides being used as the additive material in co-pyrolysis, some wastes are also needed for the recycling process. This strategy will provide a benefit of reducing the consumption of fresh raw materials for the production new plastic or tire products, which leads to saving fossil fuel.

In addition, there are some studies which have used coal in the co-pyrolysis process to produce liquid fuel, and have also showed encouraging results. Zhang et al. [92] co-pyrolyzed legume straw and Dayan lignite coal in a free fall reactor at temperatures from 500 to 700 °C. The blending ratio of biomass in mixtures varied between 0 and 100 wt%. The authors noted that the higher blending ratio of biomass may decrease the char yield, and consequently the liquid yields obtained were higher. The same tendency was also found by Aboyade et al. [51], who studied the co-pyrolysis of coal and agricultural wastes. Moreover, the rank of coal has an effect on the liquid yield. According to Wei et al. [58], the use of high-rank coal in co-pyrolysis can produce a higher liquid yield than that of low-rank coal. However, no further explanations about oil quality were found in reports of the co-pyrolysis of biomass wood and coal. For the co-pyrolysis of coal with waste tires, Kříž and Brožová reported that the increased proportion of waste tires in the pyrolysis of coal contributed to increase the liquid yield, which had a relatively lower oxygen content [143]. In addition, the type of reactor can significantly effect the oil yield quantity and quality. Acevedo et al. studied the pyrolysis of blends of coal and tire wastes in a fixed bed reactor and a rotary oven. The authors found that the oil yield was always greater in the fixed bed oven than in the rotary oven. However, the oils obtained in the rotary oven were more aromatic and contained smaller amounts of oxygenated functional groups due to their higher residence time in the hot zone of the reactor.

As shown in the above paragraph, the use of coal in co-pyrolysis can be one option to produce liquid fuel. However, this option is not a benefit with regard to reducing the dependency on fossil fuel, since coal is a part of fossil fuel. Therefore, the use of coal in the co-pyrolysis process is not recommended.

Co-pyrolysis is a promising technique that can produce a high grade pyrolysis oil from biomass waste. This technique also offers several advantages on its application:

- Co-pyrolysis can be easily applied to existing plants of the pyrolysis of biomass.
- Low cost associated with upgrading processes from pyrolysis to co-pyrolysis: if a plant is run for the pyrolysis of wood-based biomass, no money needs to be invested in a special plant for the use of waste plastics and tires.

- No special equipment needs to be designed and constructed for co-pyrolysis. Some minor modifications maybe needed, but only for the feed preparation system.
- As a byproduct, solid fuel is sometimes poor in organic matter; the addition of waste plastics and tires to wood-based biomass may improve its quality.
- The quantity and quality of desired products (oil, solid, or gas) can be easily controlled by adjusting the process parameters.
- The primary disadvantage of co-pyrolysis lies in the biomass preparation unit. Given that this technique deals with many types of biomass, an additional pre-treatment system is required, which can substantially increase the cost for the installation and operation of such units.

10. Conclusion

This review has focused on the study of co-pyrolysis techniques to produce high grade pyrolysis oil. The studies in the literature have been used to support the analysis and discussion in this paper. Many researchers have recognized that the co-pyrolysis technique can significantly improve the quantity and quality of pyrolysis oil without the presence of any catalysts or solvents and free hydrogen pressure. Therefore, this technique can be considered a simple, cheap, and effective method to obtain high-grade pyrolysis oil. Moreover, this technique also benefits to increase the caloric value of char and gas as byproducts of co-pyrolysis. As the additive material in co-pyrolysis, the availability of plastic waste and tire waste is plays an important role in the sustainability of this technique. From an economic point of view, co-pyrolysis is found to be a promising option in biomass conversion to produce pyrolysis oil. Due to the fact that biomass wastes are easy to find and available in abundant amounts around the world, co-pyrolysis has huge potential for development in many countries. In addition, by using this method, the volume of biomass wastes can be easily controlled. Using biomass wastes to produce pyrolysis oil could reduce the need for landfills, decrease the cost of waste treatment, and solve some environmental problems. Furthermore, it can also be noted that this is an optional solution to increase energy security of the nation and reduce dependence on fossil fuels.

Acknowledgements

References

[1] Shafiee S, Topal E. When will fossil fuel reserves be diminished? Energy Policy 2009;37:181–9.
[2] Manzano-Agugliaro F, Alcayde A, Montoya FG, Zapata-Sierra A, Gil C. Scientific production of renewable energies worldwide: An overview. Renew Sust Energy Rev 2013;18:134–43.
[3] Moreira JXC. Global biomass energy potential. Mitig Adapt Strat Glob Change 2006;11:313–33.
[4] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Prog Energy Combust Sci 2007;33:233–71.
[5] Krupa V, An Li STGJJPG. Introduction to the Book Series. Developments in Environmental Science. Elsevier; 2007. p. xiii–xiv.
[6] Kalogirou SA. Solar thermal collectors and applications. Prog Energy Combust Sci 2004;30:231–95.
[7] Easterly JL, Burnham M. Overview of biomass and waste fuel resources for power production. Biomass Bioenergy 1996;10:79–92.
[8] Bildirici ME. Economic growth and biomass energy. Biomass Bioenergy 2013;50:19–24.
[9] Ahtikoski A, Heikkilä J, Alenius V, Siren M. Economic viability of utilizing biomass energy from young stands – the case of Finland. Biomass Bioenergy 2008;32:988–96.
[10] Bridgwater T. Biomass for energy. J Sci Food Agric 2006;86:1755–68.
[11] Guillain M, Fairouz K, Mar SR, Monique F, Jacques LD. Attrition-free pyrolysis to produce bio-oil and char. Bioresour Technol 2009;100:6069–75.

[12] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Org Geochem 1999;30:1479–93.

[13] Vitolo S, Seggiani M, Frediani P, Ambrosini G, Politi L. Catalytic upgrading of pyrolytic oils to fuel over different zeolites. Fuel 1999;78:1147–59.

[14] Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils-state of the art for the end users. Energy Fuel 1999;13:914–21.

[15] Parihar MF, Kamil M, Goyal HB, Gupta AK, Bhatnagar AK. An experimental study on pyrolysis of biomass. Process Saf Environ Prot 2007;85:458–65.

[16] Lu Q, Li W-Z, Zhu X-F. Overview of fuel properties of biomass fast pyrolysis oils. Energy Convers Manage 2009;50:1376–83.

[17] Hew KL, Tamidi AM, Yusup S, Lee KT, Ahmad MM. Catalytic cracking of bio-oil to organic liquid product (OLP). Bioresour Technol 2010;101:8855–8.

[18] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Convers Manage 2007;48:87–92.

[19] Scheirs J. Overview of commercial pyrolysis processes for waste plastics. feedstock recycling and pyrolysis of waste plastics. John Wiley & Sons, Ltd.; 2006. p. 381–433.

[20] Toba M, Abe Y, Kuramochi H, Osako M, Mochizuki T, Yoshimura Y. Hydrodeoxygenation of waste vegetable oil over sulfide catalysts. Catal Today 2011;164:533–7.

[21] Joshi N, Lawal A. Hydrodeoxygenation of pyrolysis oil in a microreactor. Chem Eng Sci 2012;74:1–8.

[22] Panda AK, Singh RK, Mishra DK. Thermolysis of waste plastics to liquid fuel: a suitable method for plastic waste management and manufacture of value added products-A world prospective. Renew Sust Energy Rev 2010;14:233–48.

[23] Martínez JD, Veses A, Mastral AM, Murillo R, Navarro MV, Puy N, et al. Co-pyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. Fuel Process Technol 2014;119:263–71.

[24] Önal E, Uzun BB, Pütün AE. Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene. Energy Convers Manage 2014;78:704–10.

[25] Garforth AA, Ali S, Hernández-Martínez JS, Akah A. Feedstock recycling of polymer wastes. Curr Opin Solid State Mater Sci 2004;8:419–25.

[26] Kuppens T, Cornelissen T, Carleer R, Yperman J, Schreurs S, Jans M, et al. Economic assessment of flash co-pyrolysis of short rotation coppice and biopolymer waste streams. J Environ Manage 2010;91:2736–47.

[27] Veses A, Aznar M, Martínez I, Martínez JD, López JM, Navarro MV, et al. Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts. Bioresour Technol 2014;162:250–8.

[28] Venderbosch RH, Prins W. Fast pyrolysis of biomass for energy and chemicals: technologies at various scales. Sustainable development in the process industries. John Wiley & Sons, Inc.; 2010. p. 109–55.

[29] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 2012;38:68–94.

[30] Acıkgoz C, Onay O, Kockar OM. Fast pyrolysis of linseed: product yields and compositions. J Anal Appl Pyrol 2004;71:417–29.

[31] Abnisa F, Wan Daud WMA, Sahu JN. Optimization and characterization studies on bio-oil production from palm shell by pyrolysis using response surface methodology. Biomass Bioenergy 2011;35:3604–16.

[32] Pütün AE, Apaydın E, Pütün E. Rice straw as a bio-oil source via pyrolysis and steam pyrolysis. Energy 2004;29:2171–80.

[33] Demiral İ, Şensöz S. Fixed-bed pyrolysis of hazelnut (*Corylus Avellana* L.) bagasse: influence of pyrolysis parameters on product yields. Energy Source Part A 2006;28:1149–58.

[34] Vamvuka D. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—an overview. Int J Energy Res 2011;35:835–62.

[35] Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. Renew Sust Energy Rev 2000;4:1–73.

[36] Akhtar J, Saidina Amin N. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. Renew Sust Energy Rev 2012;16:5101–9.

[37] Velghe I, Carleer R, Yperman J, Schreurs S. Study of the pyrolysis of municipal solid waste for the production of valuable products. J Anal Appl Pyrol 2011;92:366–75.

[38] Bridgwater AV. Principles and practice of biomass fast pyrolysis processes for liquids. J Anal Appl Pyrol 1999;51:3–22.

[39] Sharypov VI, Marin N, Beregovtsova NG, Baryshnikov SV, Kuznetsov BN, Cebolla VL, et al. Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases. J Anal Appl Pyrol 2002;64:15–28.

[40] Abnisa F, Wan Daud WMA, Ramalingam S, Azemi MNBM, Sahu JN. Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesis liquid fuel. Fuel 2013;108:311–8.

[41] Venderbosch RH, Prins W. Fast pyrolysis technology development. Biofuel Bioprod Biorg 2010;4:178–208.

[42] Isahak WNRW, Hisham MWM, Yarmo MA, Yun Hin T-Y. A review on bio-oil production from biomass by using pyrolysis method. Renew Sust Energy Rev 2012;16:5910–23.

[43] Cao Q, Jin LE, Bao W, Lv Y. Investigations into the characteristics of oils produced from co-pyrolysis of biomass and tire. Fuel Process Technol 2009;90:337–42.

[44] Önal E, Uzun BB, Pütün AE. An experimental study on bio-oil production from co-pyrolysis with potato skin and high-density polyethylene (HDPE). Fuel Process Technol 2012;104:365–70.

[45] Liu W-J, Tian K, Jiang H, Zhang X-S, Yang G-X. Preparation of liquid chemical feedstocks by co-pyrolysis of electronic waste and biomass without

[46] Abnisa F, Daud WMAW, Sahu JN. Pyrolysis of mixtures of palm shell and polystyrene: an optional method to produce a high-grade of pyrolysis oil. Environ Prog Sust Energy 2014;33:1026–33.

[47] Jeon M-J, Choi S, Yoo K-S, Ryu C, Park S, Lee J, et al. Copyrolysis of block polypropylene with waste wood chip. Korean J Chem Eng 2011;28:497–501.

[48] Fei J, Zhang J, Wang F, Wang J. Synergistic effects on co-pyrolysis of lignite and high-sulfur swelling coal. J Anal Appl Pyrol 2012;95:61–7.

[49] Zaman AU. Comparative study of municipal solid waste treatment technologies using life cycle assessment method. Int J Environ Sci Technol 2010;7:225–34.

[50] Brebu M, Ucar S, Vasile C, Yanik J. Co-pyrolysis of pine cone with synthetic polymers. Fuel 2010;89:1911–8.

[51] Aboyade AO, Carrier M, Meyer EL, Knoetze H, Görgens JF. Slow and pressurized co-pyrolysis of coal and agricultural residues. Energy Convers Manage 2013;65:198–207.

[52] García-Pèrez M, Chaala A, Roy C. Co-pyrolysis of sugarcane bagasse with petroleum residue. Part II. Product yields and properties. Fuel 2002;81:893–907.

[53] Sánchez ME, Martínez O, Gómez X, Morán A. Pyrolysis of mixtures of sewage sludge and manure: a comparison of the results obtained in the laboratory (semi-pilot) and in a pilot plant. Waste Manage 2007;27:1328–34.

[54] Ye JL, Cao Q, Zhao YS. Co-pyrolysis of polypropylene and biomass. Energy Source Part A 2008;30:1689–97.

[55] Cordella M, Berrueco C, Santarelli F, Paterson N, Kandiyoti R, Millan M. Yields and ageing of the liquids obtained by slow pyrolysis of sorghum, switchgrass and corn stalks. J Anal Appl Pyrol 2013;104:316–24.

[56] Ateş F. Co-pyrolytic behaviors of agricultural wastes. Energy Source Part A 2011;34:111–21.

[57] Samanya J, Hornung A, Apfelbacher A, Vale P. Characteristics of the upper phase of bio-oil obtained from co-pyrolysis of sewage sludge with wood, rapeseed and straw. J Anal Appl Pyrol 2012;94:120–5.

[58] Wei L-G, Zhang L, Xu S-P. Effects of feedstock on co-pyrolysis of biomass and coal in a free-fall reactor. J Fuel Chem Technol 2011;39:728–34.

[59] Kar Y. Co-pyrolysis of walnut shell and tar sand in a fixed-bed reactor. Bioresour Technol 2011;102:9800–5.

[60] Pinto F, Paradela F, Gulyurtlu I, Ramos AM. Prediction of liquid yields from the pyrolysis of waste mixtures using response surface methodology. Fuel Process Technol 2013;116:271–83.

[61] Haykiri-Acma H, Yaman S. Interaction between biomass and different rank coals during co-pyrolysis. Renew Energy 2010;35:288–92.

[62] Sharma S, Ghoshal AK. Study of kinetics of co-pyrolysis of coal and waste LDPE blends under argon atmosphere. Fuel 2012;89:3943–51.

[63] Kabakcı SB, Aydemir H. Pyrolysis of olive pomace and copyrolysis of olive pomace with refuse derived fuel. Environ Prog Sust Energy 2013. n/a–n/a.

[64] Paradela F, Pinto F, Ramos AM, Gulyurtlu I, Cabrita I. Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes. J Anal Appl Pyrol 2009;85:392–8.

[65] Miranda M, Cabrita I, Pinto F, Gulyurtlu I. Mixtures of rubber tyre and plastic wastes pyrolysis: a kinetic study. Energy 2013;58:270–82.

[66] Zevenhoven R, Axelsen EP, Hupa M. Pyrolysis of waste-derived fuel mixtures containing PVC. Fuel 2002;81:507–10.

[67] Williams EA, Williams PT. The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor. J Chem Technol Biot 1997;70:9–20.

[68] Ohmukai Y, Hasegawa I, Mae K. Pyrolysis of the mixture of biomass and plastics in countercurrent flow reactor Part I: experimental analysis and modeling of kinetics. Fuel 2008;87:3105–11.

[69] Rotliwala YC, Parikh PA. Study on thermal co-pyrolysis of jatropha deoiled cake and polyolefins. Waste Manage Res 2011;29:1251–61.

[70] Weiland NT, Means NC, Morreale BD. Product distributions from isothermal co-pyrolysis of coal and biomass. Fuel 2012;94:563–70.

[71] Cornelissen T, Jans M, Yperman J, Reggers G, Schreurs S, Carleer R. Flash co-pyrolysis of biomass with polyhydroxybutyrate: Part 1. Influence on bio-oil yield, water content, heating value and the production of chemicals. Fuel 2008;87:2523–32.

[72] Buekens AG, Schoeters JG. Technical methods in plastics pyrolysis. Macromol Symp 1998;135:63–81.

[73] Martínez JD, Puy N, Murillo R, García T, Navarro MV, Mastral AM. Waste tyre pyrolysis – a review. Renew Sust Energy Rev 2013;23:179–213.

[74] Ghosh T, Prelas M. Petroleum. Energy Resources and Systems. Netherlands: Springer; 2009. p. 383–451.

[75] PlasticsEurope. Plastics – the Facts 2010: An analysis of Eropean plastics production, demand and recovery for 2009; 2010.

[76] PlasticsEurope. Plastics – the Facts 2011: an analysis of Eropean plastics production, demand and recovery for 2010; 2011.

[77] Crain_Communications_Inc. Tire Production by Country Rubber & Plastics News, <http://www.rubbernews.com/article/TB/20090201/STATISTICS/121019919/tire-production-by-country> (accessed 29 october 2013).

[78] Malaysian_Government. Malaysian Rubber Board, Natural rubber statistic 2012 <http://www.lgm.gov.my/nrstat/nrstats.pdf> (accessed 29 october 2013).

[79] Williams PT. Pyrolysis of waste tyres: a review. Waste Manage 2013;33:1714–28.

[80] Quek A, Balasubramanian R. Liquefaction of waste tires by pyrolysis for oil and chemicals – a review. J Anal Appl Pyrol 2013;101:1–16.

[81] Cornelissen T, Jans M, Stals M, Kuppens T, Thewys T, Janssens GK, et al. Flash co-pyrolysis of biomass: the influence of biopolymers. J Anal Appl Pyrol 2009;85:87–97.

[82] Cornelissen T, Yperman J, Reggers G, Schreurs S, Carleer R. Flash co-pyrolysis of biomass with polylactic acid. Part 1: Influence on bio-oil yield and heating value. Fuel 2008;87:1031–41.

[83] Paradela F, Pinto F, Gulyurtlu I, Cabrita I, Lapa N. Study of the co-pyrolysis of biomass and plastic wastes. Clean Technol Environ 2009;11:115–22.

[84] Rutkowski P, Kubacki A. Influence of polystyrene addition to cellulose on chemical structure and properties of bio-oil obtained during pyrolysis. Energy Convers Manage 2006;47:716–31.

[85] Rutkowski P. Influence of zinc chloride addition on the chemical structure of bio-oil obtained during co-pyrolysis of wood/synthetic polymer blends. Waste Manage 2009;29:2983–93.

[86] Szuba J, Michalik L. Co-pyrolysis as a method of upgrading some products of coal processing. Fuel 1982;61:1201–6.

[87] Alias R, Hamid KHK, Ismail KN. Co-pyrolysis and catalytic co-pyrolysis of waste tyres with oil palm empty fruit bunches. J Appl Sci 2011;11:2448–51.

[88] Önenç S, Brebu M, Vasile C, Yanik J. Copyrolysis of scrap tires with oily wastes. J Anal Appl Pyrol 2012;94:184–9.

[89] Uçar S, Karagöz S, Yanik J, Saglam M, Yuksel M. Copyrolysis of scrap tires with waste lubricant oil. Fuel Process Technol 2005;87:53–8.

[90] Siva M, Onenc S, Uçar S, Yanik J. Influence of oily wastes on the pyrolysis of scrap tire. Energy Convers Manage 2013;75:474–81.

[91] Johannes I, Tiikma L, Luik H. Synergy in co-pyrolysis of oil shale and pine sawdust in autoclaves. J Anal Appl Pyrol 2013;104:341–52.

[92] Zhang L, Xu S, Zhao W, Liu S. Co-pyrolysis of biomass and coal in a free fall reactor. Fuel 2007;86:353–9.

[93] Zhou L, Wang Y, Huang Q, Cai J. Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis. Fuel Process Technol 2006;87: 963–9.

[94] Wang G, Li A. Thermal decomposition and kinetics of mixtures of polylactic acid and biomass during copyrolysis. Chinese J Chem Eng 2008;16:929–33.

[95] Demirbas A. Pyrolysis mechanisms of biomass materials. Energy Source Part A 2009;31:1186–93.

[96] Jakab E, Várhegyi G, Faix O. Thermal decomposition of polypropylene in the presence of wood-derived materials. J Anal Appl Pyrol 2000;56:273–85.

[97] Jakab E, Blazsó M, Faix O. Thermal decomposition of mixtures of vinyl polymers and lignocellulosic materials. J Anal Appl Pyrol 2001;58–59:49–62.

[98] Sun J-P, Sui S-J, Zhang Z-J, Tan S, Wang Q-W. Study on the pyrolytic behavior of wood-plastic composites using Py-GC/MS. BioResources 2013; 8:6196–210.

[99] Kreith F. The CRC handbook of mechanical engineering. 2nd ed. CRC Press, Inc.; 1998.

[100] Asadullah M, Anisur Rahman M, Mohsin Ali M, Abdul Motin M, Borhanus Sultan M, Robiul Alam M, et al. Jute stick pyrolysis for bio-oil production in fluidized bed reactor. Bioresour Technol 2008;99:44–50.

[101] Omar R, Idris A, Yunus R, Khalid K, Aida Isma MI. Characterization of empty fruit bunch for microwave-assisted pyrolysis. Fuel 2011;90:1536–44.

[102] Fahmi R, Bridgwater AV, Donnison I, Yates N, Jones JM. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. Fuel 2008;87:1230–40.

[103] Qu T, Guo W, Shen L, Xiao J, Zhao K. Experimental study of biomass pyrolysis based on three major components: hemicellulose, cellulose, and lignin. Ind Eng Chem Res 2011;50:10424–33.

[104] Wu C, Wang Z, Huang J, Williams PT. Pyrolysis/gasification of cellulose, hemicellulose and lignin for hydrogen production in the presence of various nickel-based catalysts. Fuel 2013;106:697–706.

[105] Yu H, Zhang Z, Li Z, Chen D. Characteristics of tar formation during cellulose, hemicellulose and lignin gasification. Fuel 2014;118:250–6.

[106] Kang S, Li X, Fan J, Chang J. Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, d-xylose, and wood meal. Ind Eng Chem Res 2012;51:9023–31.

[107] Zannikos F, Kalligeros S, Anastopoulos G, Lois E. Converting biomass and waste plastic to solid fuel briquettes. J Renew Energy 2013;2013:9.

[108] Heikkinen JM, Hordijk JC, de Jong W, Spliethoff H. Thermogravimetry as a tool to classify waste components to be used for energy generation. J Anal Appl Pyrol 2004;71:883–900.

[109] Ahmad I, Ismail Khan M, Ishaq M, Khan H, Gul K, Ahmad W. Catalytic efficiency of some novel nanostructured heterogeneous solid catalysts in pyrolysis of HDPE. Polym Degrad Stabil 2013;98:2512–9.

[110] Hong S-J, Oh SC, Lee H-P, Kim HT, Yoo K-O. A Study on the pyrolysis characteristics of poly(vinyl chloride). J Korean Inst Chem Eng 1999;37: 515–21.

[111] Park SS, Seo DK, Lee SH, Yu T-U, Hwang J. Study on pyrolysis characteristics of refuse plastic fuel using lab-scale tube furnace and thermogravimetric analysis reactor. J Anal Appl Pyrol 2012;97:29–38.

[112] Aboulkas A, El harfi K, El Bouadili A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. Energy Convers Manage 2010;51:1363–9.

[113] Jung S-H, Cho M-H, Kang B-S, Kim J-S. Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. Fuel Process Technol 2010;91:277–84.

[114] Othman N, Basri NEA, Yunus MNM, Sidek LM. Determination of physical and chemical characteristics of electronic plastic waste (Ep-Waste) resin using proximate and ultimate analysis method. In: International conference on construction and building technology; 2008. p. 169–80.

[115] Demirbas A. Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. J Anal Appl Pyrol 2004;72:97–102.

[116] Kiran N, Ekinci E, Snape CE. Recyling of plastic wastes via pyrolysis. Resour Conserv Recycl 2000;29:273–83.

[117] Kaminsky W. Recycling of polymeric materials by pyrolysis. Makromol Chemie-M Symp 1991;48–49:381–93.

[118] Ucar S, Karagoz S, Ozkan AR, Yanik J. Evaluation of two different scrap tires as hydrocarbon source by pyrolysis. Fuel 2005;84:1884–92.

[119] Guldogan Y, Bozdemir TO, Durusoy T. Effect of heating rate on pyrolysis kinetics of tuncbilek lignite. Energy Source 2000;22:305–12.

[120] Paethanom A, Yoshikawa K. Influence of pyrolysis temperature on rice husk char characteristics and its tar adsorption capability. Energies 2012;5: 4941–51.

[121] Azeez AM, Meier D, Odermatt J. Temperature dependence of fast pyrolysis volatile products from European and African biomasses. J Anal Appl Pyrol 2011;90:81–92.

[122] Pan YG, Velo E, Puigjaner L. Pyrolysis of blends of biomass with poor coals. Fuel 1996;75:412–8.

[123] Westerhof RJM, Kuipers NJM, Kersten SRA, van Swaaij WPM. Controlling the water content of biomass fast pyrolysis oil. Ind Eng Chem Res 2007;46: 9238–47.

[124] Yu F, Deng S, Chen P, Liu Y, Wan Y, Olson A, et al. Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover. Appl Biochem Biotech 2007;137–140:957–70.

[125] Diebold JP. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. NREL/SR-570-27613 2000; Colorado, USA.

[126] Brebu M, Spiridon I. Co-pyrolysis of LignoBoost® lignin with synthetic polymers. Polym Degrad Stabil 2012;97:2104–9.

[127] Aboulkas A, Makayssi T, Bilali L, El harfi K, Nadifiyine M, Benchanaa M. Co-pyrolysis of oil shale and High density polyethylene: structural characterization of the oil. Fuel Process Technol 2012;96:203–8.

[128] Abnisa F, Arami-Niya A, Wan Daud WMA, Sahu JN, Noor IM. Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis. Energy Convers Manage 2013;76:1073–82.

[129] Abnisa F, Arami-Niya A, Daud WMAW, Sahu JN. Characterization of bio-oil and bio-char from pyrolysis of palm oil wastes. BioEnergy Res 2013;6: 830–40.

[130] Ali MF, Al-Malki A, El-Ali B, Martinie G, Siddiqui MN. Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques. Fuel 2006;85:1354–63.

[131] Bernardo M, Lapa N, Gonçalves M, Mendes B, Pinto F, Fonseca I, et al. Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures. J Hazard Mater 2012;219–220:196–202.

[132] López A, de Marco I, Caballero BM, Laresgoiti MF, Adrados A. Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. Fuel Process Technol 2011;92:253–60.

[133] Kim J-S, Kaminsky W, Schlesselmann B. Pyrolysis of a fraction of mixed plastic wastes depleted in PVC. J Anal Appl Pyrol 1997;40–41:365–72.

[134] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuel 2006;20:848–89.

[135] Williams PT, Williams EA. Interaction of plastics in mixed-plastics pyrolysis. Energy Fuel 1998;13:188–96.

[136] Hester RE, Harrison RM. Waste as a resource. issues in environmental science and technology, Royal Society of Chemistry, Cambridge, 2013, 37.

[137] Vanreppelen K, Kuppens T, Thewys T, Carleer R, Yperman J, Schreurs S. Activated carbon from co-pyrolysis of particle board and melamine (urea) formaldehyde resin: a techno-economic evaluation. Chem Eng J 2011;172:835–46.

[138] Graham JR, Harvey CR. The theory and practice of corporate finance: evidence from the field. J Financ Econ 2001;60:187–243.

[139] Pasqual J, Padilla E, Jadotte E. Technical note: Equivalence of different profitability criteria with the net present value. Int J Prod Econ 2013;142: 205–10.

[140] Aziz RF. Optimizing strategy for repetitive construction projects within multi-mode resources. Alexandria Eng J 2013;52:67–81.

[141] Shelley MD, El-Halwagi MM. Techno-economic feasibility and flowsheet synthesis of scrap tire/plastic waste liquefaction. J Elastom Plast 1999;31:232–54.

[142] Huffman GP, Shah N. Feasibility study for a demonstration plant for liquefaction and coprocessing of waste plastics and tires. ChemTech 1998;28:34–41.

[143] Kříž V, Brožová Z. Co-pyrolysis of coal/waste polymers mixtures. Acta Geodyn Geomater 2007;4:39–42.